



# Strong effect of multi-electron oxygen reduction reaction on photocatalysis through the promotion of interfacial charge transfer

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## ABSTRACT

An efficient visible-light-driven photocatalyst with interface charge transfer (IFCT) effect was achieved by assembling Fe-porphyrin based conjugated microporous polymer on TiO<sub>2</sub> microspheres. It was revealed that IFCT effect played a crucial role in the enhancement of photocatalytic performance. In addition, the oxygen reduction reaction (ORR) activity of TiO<sub>2</sub> was enhanced in the presence of Fe-porphyrin based conjugated microporous polymer and IFCT effect was promoted obviously due to the high ORR activity. It's speculated that multi-electron ORR could accelerate the consumption of photoinduced electrons, retarding the recombination of photoinduced holes and electrons in the IFCT process, leaving more high-oxidizing photoinduced holes in the valance band of TiO<sub>2</sub> for further degradation. What's more, to further clarify the relationship between multi-electron ORR and IFCT effect, the influence of electron transfer number on the generation of photoinduced holes in the IFCT process was studied, and it was believable that four-electron oxygen reduction process was better able to accelerate the generation of photoinduced holes in the IFCT process than two-electron oxygen reduction process, resulting in higher photocatalytic activity.

## 1. Introduction

Semiconductor-based photocatalysis has been considered as one of the most important technologies for organic pollutant degradation and hydrogen production. Although wide-band gap semiconductors, such as TiO<sub>2</sub>, ZnO and SrTiO<sub>3</sub>, are considered as efficient photocatalysts owing to the high redox potential of photogenerated charge carries, they could only be excited under UV irradiation [1,2]. Heterogeneous photocatalysis with wide-band gap semiconductors presents a promising approach for efficiently utilizing solar energy, owing to much higher quantum efficiency compared to pristine semiconductors [3–5]. Some mechanisms for heterogeneous visible-light-induced photocatalysis, such as Z-scheme photocatalysis [6] and IFCT effect [7], have been proposed as further design guides for photocatalysts with high solar energy conversion.

IFCT effect has been demonstrated to be an efficient way for enhancing the separation of photoinduced electron–holes. Recently, Hashimoto group successfully constructed a series of visible-light-driven photocatalysts by grafting Cu (II) or Fe (III) cluster on the surface of wide-band gap semiconductors [8–10]. In these systems, photoinduced IFCT effect from semiconductors to the grafted clusters resulted in not only the extension of the photo response from UV to visible light region, but also the efficient consumption of photoinduced electrons via

the reduction reaction of the grafted metallic clusters, simultaneously taking advantage of the high-oxidizing holes in the valance band for complete degradation of organic compounds [11]. Although electron reduction reaction of oxygen, during which the excited electrons were consumed, was found in the IFCT process, the quantum efficiency was still limited due to the weak charge separation.

In photocatalytic degradation, the oxidation of pollutants is significantly accelerated as strongly oxidizing species, such as H<sub>2</sub>O<sub>2</sub> and <sup>•</sup>O<sub>2</sub><sup>−</sup>, could be generated due to the reduction of molecular oxygen by photogenerated electrons [12–16]. Hence, it seems likely that ORR plays an important role in photocatalytic degradation. It has been reported that many microporous materials, such as metal-organic frameworks (MOFs) [17], covalent organic frameworks (COFs) [18] and conjugated microporous polymers (CMPs) [19], showed excellent ORR activity with high electron transfer number (n). Meyer et al. [20] have reported the synthesis of heme-functionalized TiO<sub>2</sub> compound, where multi-electron transfer was found from hemes to TiO<sub>2</sub> to accelerate the reductive process. As such, introducing high ORR activity to IFCT system might retard the recombination of photoinduced electron–holes, improving the quantum efficiency of the IFCT system.

Herein, Fe-porphyrin (denoted as FeP) and porphyrin based CMPs were assembled on the surface of TiO<sub>2</sub> microspheres (denoted as TiO<sub>2</sub>-FeCMP and TiO<sub>2</sub>-CMP) to prepare an efficient visible-light-driven

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photocatalyst with IFCT effect, where multi-electron ORR was found to play a vital role in the promotion of IFCT effect. It's revealed that multi-electron ORR could accelerate the consumption of photoinduced electrons in the IFCT process, where more photoinduced holes in the valance band of  $\text{TiO}_2$  were left for further degradation. What's more, the relationship between  $n$  value and the generation of photoinduced holes in the IFCT process was clarified, and it was believable that four-electron oxygen reduction process was better able to accelerate the generation of photoinduced holes in the IFCT process than two-electron oxygen reduction process, resulting in higher photocatalytic activity.

## 2. Experimental

### 2.1. Preparation

**Preparation of 5, 10, 15, 20-tetrakis (4'-bromophenyl) porphyrin (Por).** Porphyrin was prepared according to the procedure reported previously [19]. *P*-bromobenzaldehyde (5.58 g, 30 mmol) was added into the mixture of nitrobenzene (150 mL) and acetic acid (225 mL), and heated up to 120 °C, then, freshly distilled pyrrole (2.1 mL) was added and kept for 1 h. After cooling to room temperature, the as-prepared precipitate was collected by filtration and washed with methanol for several times. The product was further purified by recrystallization from chloroform and methanol twice.

**Preparation of 5, 10, 15, 20-tetrakis (4'-bromophenyl) porphyrin Ferric (FeP) [21].** The as-prepared porphyrin (1.00 g) and  $\text{FeCl}_3$  (869.2 mg) were placed in a 100 mL round-bottom flask and dried at 100 °C in vacuum overnight. Degassed DMF was added in the flask and stirred at 100 °C for 10 h. After cooling to room temperature, deionized water (200 mL) was poured into the mixture and the resulted product was filtered and washed with water and methanol. The crude product was further purified by recrystallization from chloroform and methanol twice.

**Preparation of  $\text{TiO}_2$ -FeCMP compound.** 1,5-cyclooctadiene (445  $\mu\text{L}$ ), bis (1,5-cyclooctadiene) nickel (0) (1.00 g) and 2,2'-bipyridyl (564.7 mg) were added into dehydrate dioxane (60 mL), and the mixture was kept at 100 °C for 1 h under argon atmosphere. Then, the as-prepared FeP (741.2 mg, see details in Supporting Information) was added into the mixture and stirred for 12 h before  $\text{TiO}_2$  microsphere (2.80 g, see details in Supporting Information) was added to react for another 12 h. After cooling to the room temperature, concentrated HCl (20 mL) was dropped into the mixture, and the resulted precipitate was collected by filtration and washed with aqueous saturated EDTA solution, deionized water,  $\text{CHCl}_3$  and THF, respectively. The crude product was further extracted by Soxhlet with methanol, acetone, and THF for 1 day, respectively, and dried at 100 °C under vacuum. The as-prepared product was denoted as  $\text{TiO}_2$ -FeCMP. The  $\text{TiO}_2$ -CMP was synthesized based on the as-prepared porphyrin (See details in Supporting Information) instead of FeP.

### 2.2. Characterization

X-ray diffraction (XRD) patterns of these samples were obtained in the range of 5–80° (2 $\theta$ ) using a Bruker D8 ADVANCE diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.54178 \text{ \AA}$ ). The morphologies were recorded by scanning electron microscopy (SEM, LEO 1530 VP) and transmission electron microscopy (TEM, Thermo Fisher Scientific, Tecnai-G20, 200 kV, USA). Fourier transform-infrared spectra (FT-IR) were recorded by infrared spectrometer (Bruker, Vector 33). UV–vis diffuse reflectance spectra were performed in a Hitachi Corporation UV-3010 spectrophotometer, using  $\text{BaSO}_4$  as the reflectance standard. Nitrogen adsorption-desorption isotherms were obtained from an isothermal nitrogen sorption analyzer (TriStar 3010, Micromeritics USA). Surface chemical compositions and chemical status of the as-prepared samples were analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Fisher Scientific, USA). Electron spin resonance (ESR) spectra

were conducted on a JEOL JES FA200 spectrometer.

### 2.3. Photocatalytic performance

The degradation of methyl orange (MO) solution ( $10 \text{ mg L}^{-1}$ ) was carried out to evaluate the photocatalytic performance of as-prepared samples under visible light irradiation. 30 mg of catalyst sample was mixed with 30 mL of methyl orange solution in a water-cool reactor. Prior to the irradiation under a PLS-SXE300 Xe lamp (Beijing Perfectlight Technology Co., Ltd) equipped with cutoff filters (420 nm, 475 nm and 530 nm), the suspension was stirred magnetically for 30 min in a dark box to reach an adsorption-desorption equilibrium. About 3 mL aliquots were taken and then filtered with a microspore membrane at a certain time interval. The Shimadzu UV-2050 spectrophotometer was used to record the maximum absorbance of the filtrate (462 nm for MO).

### 2.4. Electrochemical characterization

Electrochemical measurements of cyclic voltammetry, rotating disk electrode (RDE) were performed by a computer-controlled potentiostat (CHI 660, CH Instrument, China) with a three-electrode cell system, in which a glass carbon RDE (ATA-1B, Jiangfen Electroanalytical Instrument) after loading the electrocatalysts was used as the working electrode, an Ag/AgCl (KCl, 3 M) electrode as the reference electrode, and a Pt wire as the counter electrode. The electrochemical experiments were conducted in  $\text{O}_2$  saturated 0.1 M KOH electrolyte for the oxygen reduction reaction. The potential range is cyclically scanned between  $-0.6$  and  $0 \text{ V}$  in 0.1 M KOH at a scan rate of  $100 \text{ mV s}^{-1}$  at room temperature after purging  $\text{O}_2$  or Ar gas for 15 min. RDE measurements were carried out at different rotating speeds from 400 to 2500 rpm (see details in Supporting Information).

## 3. Results and discussion

The typical absorptions of porphyrin were found in the UV–vis diffuse reflectance spectra (Fig. 1). Compared to pure  $\text{TiO}_2$  (Fig. 1a),  $\text{TiO}_2$ -FeCMP (Fig. 1c) and  $\text{TiO}_2$ -CMP (Fig. 1d) showed typical B-band (ca. 420 nm) and Q-band (between 500 nm and 700 nm) of porphyrin, which suggested that porphyrin units were introduced into the compound successfully [22,23]. What's more,  $\text{TiO}_2$ -FeCMP only had one Q-band absorption while  $\text{TiO}_2$ -CMP had two absorptions, which might be ascribed to the good symmetry due to the insert of Fe ion [24]. A broad absorption of Fe- $\text{TiO}_2$  (Fig. 1b) between 450 nm and 500 nm was observed which revealed that Fe ion was grafted on the  $\text{TiO}_2$  successfully [25]. The XRD patterns of the obtained samples (Fig. S1) were in good

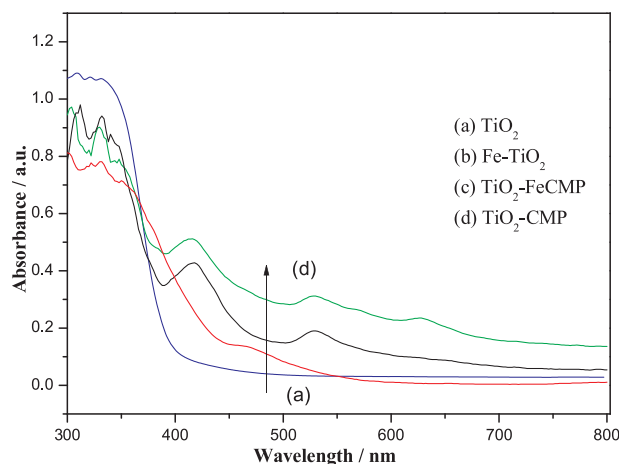


Fig. 1. UV–vis diffuse reflectance spectra.

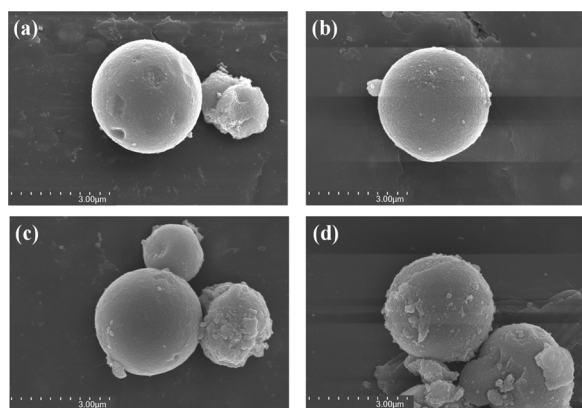


Fig. 2. SEM of (a)  $\text{TiO}_2$ , (b)  $\text{Fe-TiO}_2$ , (c)  $\text{TiO}_2\text{-FeCMP}$  and (d)  $\text{TiO}_2\text{-CMP}$ .

agreement with anatase  $\text{TiO}_2$  (PDF card No. 21-1272) and no other obvious peaks were found with the CMP added. The Fourier transform infrared (FT-IR) spectrum (Fig. S2) of  $\text{TiO}_2\text{-FeCMP}$  revealed the absence of the characteristic C-Br vibration band at  $1072\text{ cm}^{-1}$ , which illustrated that the FeP were covalently integrated into the compound [19]. Thermo gravimetric (TG) analysis (Fig. S3) showed that the content of CMP in the compound was up to 10.19%. EDX analysis indicated the presence of Ti, O, C, N and Fe (Fig. S4), and the content of Fe was up to 0.15%. These results demonstrated the successful fabrication of the  $\text{TiO}_2\text{-FeCMP}$  compound.

The morphology of the as-prepared samples were recorded by scanning electron microscopy (SEM). The SEM images (Figs. 2 and S5) revealed that pure  $\text{TiO}_2$  microspheres (Fig. 2a) were in the range of 2–5  $\mu\text{m}$ , and the incorporation of CMP made no difference on the morphology. To gain the insight into the morphology, transmission electron microscopy (TEM) was performed. As shown in Fig. 3,  $\text{TiO}_2\text{-FeCMP}$  possessed a highly mesoporous framework comprised of densely

nanoparticles, and the STEM-mappings (Fig. S4a) clearly demonstrated the core-shell structure of the  $\text{TiO}_2\text{-FeCMP}$ . Nitrogen sorption analysis (Fig. 3d) revealed that pure  $\text{TiO}_2$  microspheres had well mesoporous structure with Brunauer-Emmett-Teller (BET) surface area of  $\sim 219.4\text{ m}^2\text{ g}^{-1}$ . Although  $\text{TiO}_2$  microspheres were encapsulated by CMP in  $\text{TiO}_2\text{-CMP}$  compound, well mesoporous structures were found in both  $\text{TiO}_2\text{-FeCMP}$  and  $\text{TiO}_2\text{-CMP}$  with BET surface area of  $\sim 231.0$  and  $212.5\text{ m}^2\text{ g}^{-1}$  respectively. Well-defined mesoporous structure with a size of 3.86 nm was obtained for  $\text{TiO}_2\text{-FeCMP}$  (4.24 and 4.84 nm for  $\text{TiO}_2\text{-CMP}$  and  $\text{TiO}_2$  respectively), which confirmed the well mesoporous structure of the CMP (Fig. 3e).

X-ray photoelectron spectroscopy (XPS) analysis revealed the presence of Ti2p, O1s, N1s, C1s and Fe2p in the compound (Figs. 4 and S6). The high-resolution N1s (Fig. 4a) spectra of  $\text{TiO}_2\text{-FeCMP}$  could be fitted to three different signals that corresponded to pyridinic N and Fe-N bonding (399.48 eV, N1), pyrrolic N (400.98 eV, N2) and graphitic N (401.88 eV, N3), respectively [26,27]. The high-resolution Ti2p (Fig. 4b) showed a doublet at 458.28 eV for  $\text{Ti}2\text{p}_{3/2}$  and at 464.08 eV for  $\text{Ti}2\text{p}_{1/2}$ . In general, it's about 5.8 eV for the binding energy difference of  $\text{Ti}2\text{p}_{3/2}$  and  $\text{Ti}2\text{p}_{1/2}$ , which is ascribed to the +4 oxidation state of Ti in  $\text{TiO}_2$  [28]. However,  $\text{Ti}^{3+}2\text{p}$  could not be found remarkably, which indicated that there was no  $\text{Ti}^{3+}$  existed in the compound.

In order to evaluate the photocatalytic performance, MO was chosen as the main pollutant to degrade under visible light irradiation (Fig. 5a).  $\text{TiO}_2$  showed no response to the visible light, while  $\text{Fe-TiO}_2$  did, which was ascribed to IFCT effect from the valence band of  $\text{TiO}_2$  to the surface Fe (III) clusters (Fig. S7a). The concentration of MO were reduced by about 47.6% and 94.9% for  $\text{TiO}_2\text{-CMP}$  and  $\text{TiO}_2\text{-FeCMP}$ , respectively. Moreover,  $\text{TiO}_2\text{-FeCMP}$  also showed the highest photocatalytic activity on phenol degradation (Fig. S7b). To clarify the IFCT process, the degradation of MO over  $\text{TiO}_2\text{-CMP}$  and  $\text{TiO}_2\text{-FeCMP}$  was carried out under different cut-offs (UV, visible light,  $> 475\text{ nm}$  and  $> 530\text{ nm}$ ). As shown in Fig. 5b, there was no obvious difference in the MO removal under UV light for both  $\text{TiO}_2\text{-CMP}$  and  $\text{TiO}_2\text{-FeCMP}$ , as

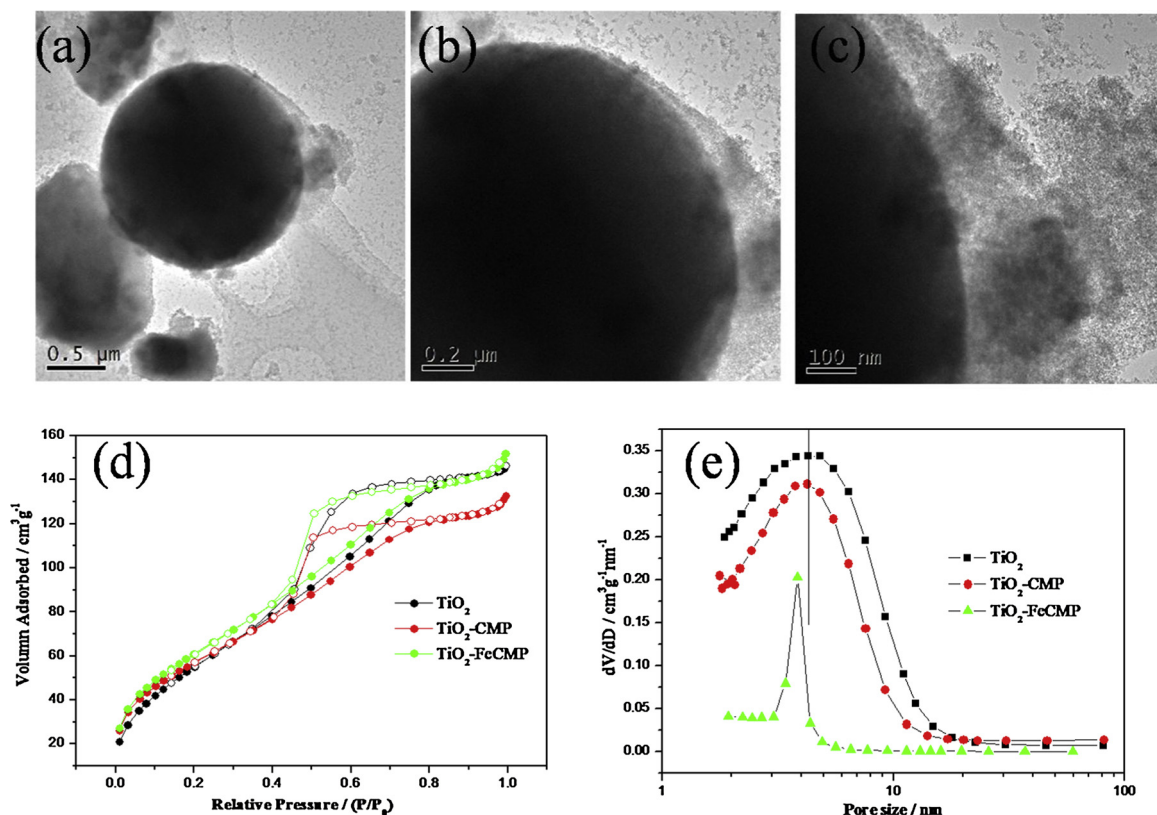


Fig. 3. (a) TEM of  $\text{TiO}_2\text{-FeCMP}$ , (b), (c) close inspection of  $\text{TiO}_2\text{-FeCMP}$ , (d) nitrogen sorption, (e) pore size distribution.

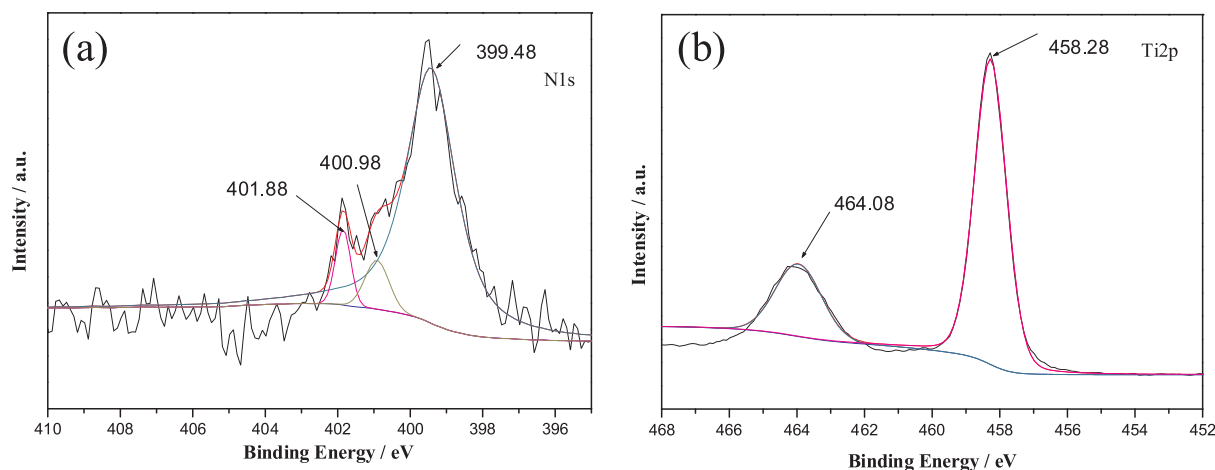


Fig. 4. XPS spectra of  $\text{TiO}_2\text{-FeCMP}$ , (a) N1s, (b) Ti2p.

the both holes in the valence band could be excited under UV light. As for visible light and  $\lambda > 475$  nm, the MO removal fell inconspicuously for  $\text{TiO}_2\text{-FeCMP}$ , while for  $\lambda > 530$  nm, the removal dropped sharply from 82.2% to 12.6%, which confirmed the IFCT effect in the  $\text{TiO}_2\text{-FeCMP}$  compound. It was speculated that IFCT was triggered by assembling FeP based conjugated microporous polymers on  $\text{TiO}_2$  microspheres.

To further confirm IFCT process in the  $\text{TiO}_2\text{-FeCMP}$ , the  $\text{DMPO}\cdot\text{CH}_2\text{OH}$  spin adducts formed in the visible light irradiated methanol and 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) suspensions of  $\text{TiO}_2\text{-FeCMP}$  and  $\text{TiO}_2\text{-CMP}$  in the absence of oxygen were recorded by ESR measurements [11] (Fig. 6, see details in Text S7). In the case of  $\text{TiO}_2\text{-FeCMP}$  (Fig. 6a), the characteristic ESR sextet peaks of the  $\text{DMPO}\cdot\text{CH}_2\text{OH}$  spin adducts were found, and the intensities of sextet peaks increased under visible light irradiation. As for  $\text{TiO}_2\text{-CMP}$  (Fig. 6b), no ESR signals were observed even under visible light irradiation. This indicated that the photoinduced holes in the valence band of  $\text{TiO}_2$  could be effectively generated over  $\text{TiO}_2\text{-FeCMP}$  under visible light irradiation. It was obvious that IFCT effect could be triggered from the valence band of  $\text{TiO}_2$  to the Fe (III) in the FeCMP. Furthermore, compared with  $\text{Fe-TiO}_2$  (Fig. S7c), much more photoinduced holes could be generated, which demonstrated the importance of CMP structure.

Moreover, it was revealed from the trapping experiments (Fig. S8) that  $\cdot\text{OH}$ ,  $\text{h}^+$  and  $\cdot\text{O}_2^-$  had different influence on the degradation results and  $\text{h}^+$  was the most critical species. It seemed feasible that IFCT process was supposed to be the main reason for the higher photocatalytic activity of  $\text{TiO}_2\text{-FeCMP}$ , while the photocatalytic activity of

$\text{TiO}_2\text{-CMP}$  was ascribed for the  $\cdot\text{O}_2^-$ . However, the MO removal of  $\text{TiO}_2\text{-FeCMP}$  under argon ambient (Fig. S9) dropped from 94.9% to 26.6%, which suggested that  $\text{O}_2$  behavior might be bound up with IFCT effect. It was speculated that multi-electron ORR might promote the IFCT process, resulting in higher photocatalytic activity.

In order to investigate the relationship between ORR and IFCT process,  $\text{TiO}_2\text{-FeCMP}$  with different reaction time were prepared (Text S9), which were denoted as  $\text{TiO}_2\text{-FeCMP0}$ ,  $\text{TiO}_2\text{-FeCMP6}$  and  $\text{TiO}_2\text{-FeCMP18}$  (Fig. S10, Supporting information). Moreover, electrochemical measurements were employed to gain further insight into the photocatalytic mechanism. Cyclic voltammetry (CV) in  $\text{N}_2$  and  $\text{O}_2$  saturated 0.1 M KOH was employed to examine the ORR catalytic activity of  $\text{TiO}_2\text{-FeCMP}$  series at a scan rate of  $100 \text{ mV s}^{-1}$  (Figs. 7a and S12). In the  $\text{N}_2$  saturated solution, a featureless slope for the cathodic current was presented for all of the CV curves within the entire potential range. Whereas, a well-defined cathodic current peak was found at all of the CV curves in the  $\text{O}_2$  saturated electrolyte, suggesting a prominent ORR activity for  $\text{TiO}_2\text{-FeCMP}$  series. Moreover, rotating-disk electrode (RDE) measurements in 0.1 M KOH saturated with  $\text{O}_2$  were performed on  $\text{TiO}_2\text{-FeCMP}$  series (Figs. 7b and S13). According to the Koutecky-Levich equation (See Supporting Information for detail), the electron transfer number ( $n$ ) of  $\text{TiO}_2\text{-FeCMP}$  was calculated to be 3.32 at 0.45 to 0.5 V vs. RHE (Fig. 8), suggesting a mainly four-electron oxygen reduction process. And for  $\text{TiO}_2\text{-FeCMP6}$ , the  $n$  value was calculated to be 2.39, containing both two-electron oxygen reduction process and four-electron oxygen reduction process (Fig. S15b). In contrast,  $\text{TiO}_2\text{-FeCMP0}$  and  $\text{TiO}_2\text{-FeCMP18}$  exhibited much lower  $n$  values of 1.83 and 2.07, which were ascribed to a two-electron oxygen reduction process

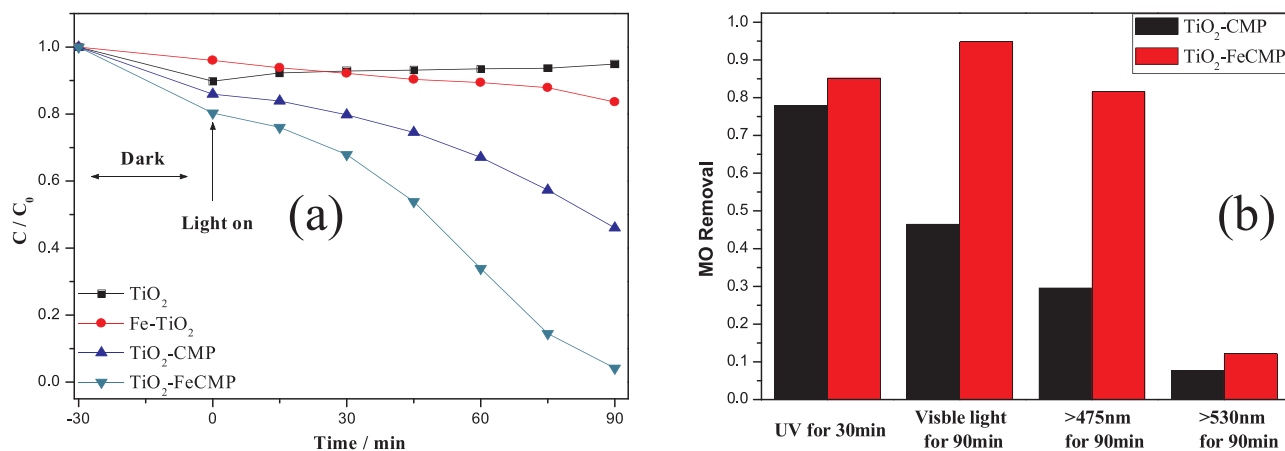


Fig. 5. (a) Photocatalytic degradation curves of MO, (b) photocatalytic degradation under different cut-offs.



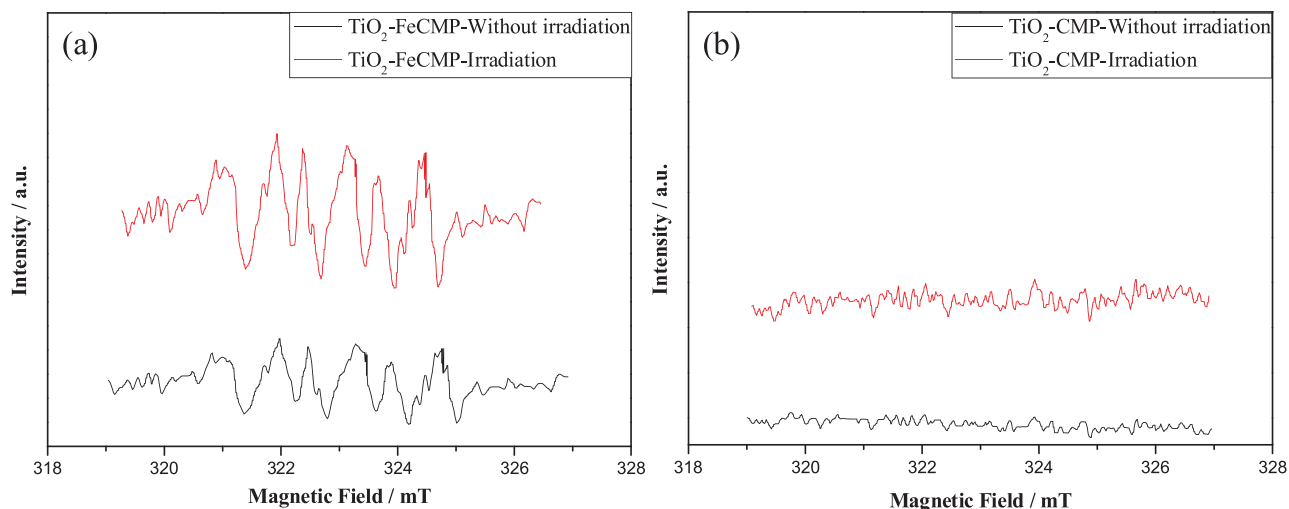


Fig. 6. ESR spectra of (a)  $\text{TiO}_2\text{-FeCNP}$ , (b)  $\text{TiO}_2\text{-CNP}$ .

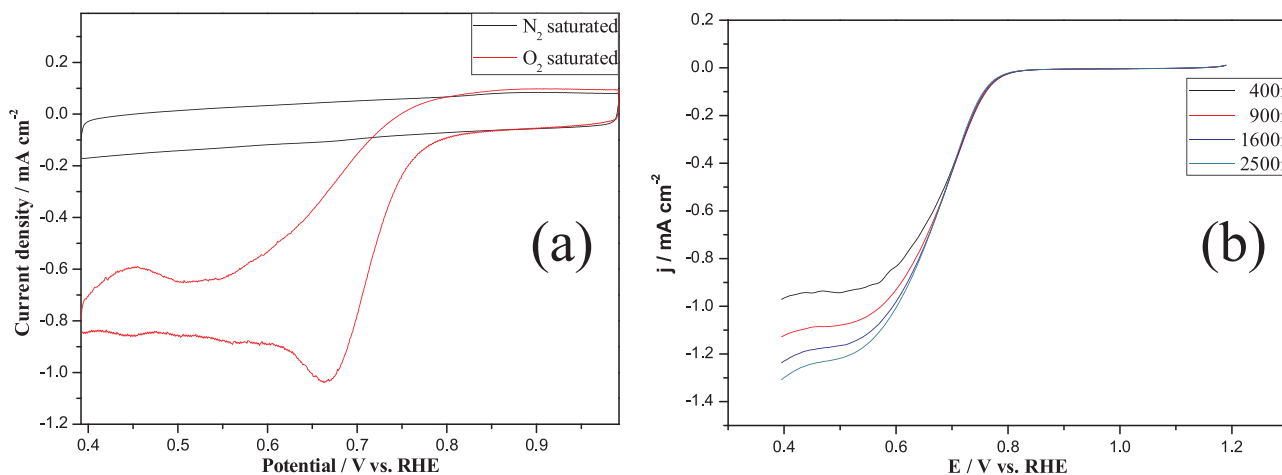


Fig. 7. (a) Cyclic voltammetry of  $\text{TiO}_2\text{-FeCNP}$ , (b) LSV curves of  $\text{TiO}_2\text{-FeCNP}$  at different rotation rates in  $\text{O}_2$ -saturated 0.1 M KOH.

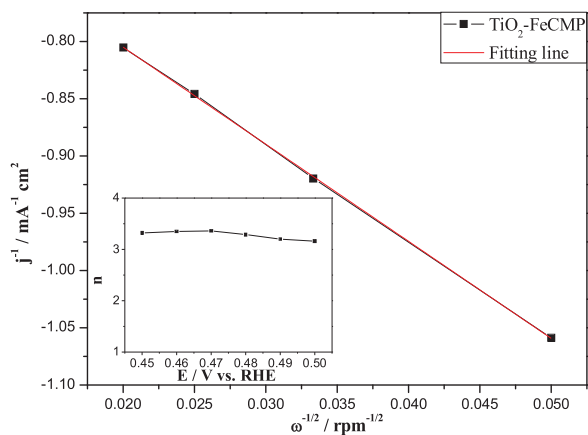


Fig. 8. Koutecky-Levich plots of  $\text{TiO}_2\text{-FeCNP}$  at 0.45 V, the inset shows the dependence of electron transfer numbers ( $n$ ) at different electrode potentials.

(Figs. S15a and S15c).  $\text{TiO}_2\text{-FeCNP}$  showed the highest diffusion current among the series (Fig. S14), which was consistent with the degradation results (Fig. S11). As such, it seemed feasible that multi-electron ORR played a key role in the improvement of photocatalytic performance, and four-electron oxygen reduction process was better than two-electron oxygen reduction process.

To further confirm the relationship between multi-electron ORR and

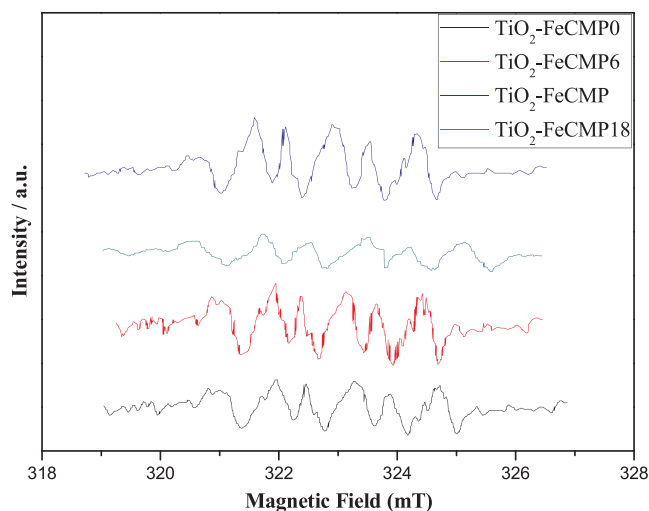


Fig. 9. ESR spectra of  $\text{TiO}_2\text{-FeCNP}$  series under visible light irradiation.

photocatalytic performance, the  $\text{DMPO}\cdot\text{CH}_2\text{OH}$  spin adducts formed in the visible light irradiated methanol suspensions of  $\text{TiO}_2\text{-FeCNP}$  series in the absence of oxygen were detected by ESR spectroscopy (Fig. 9). The characteristic ESR sextet peaks of  $\text{DMPO}\cdot\text{CH}_2\text{OH}$  spin adducts were found clearly under visible-light irradiation for  $\text{TiO}_2\text{-FeCNP}$

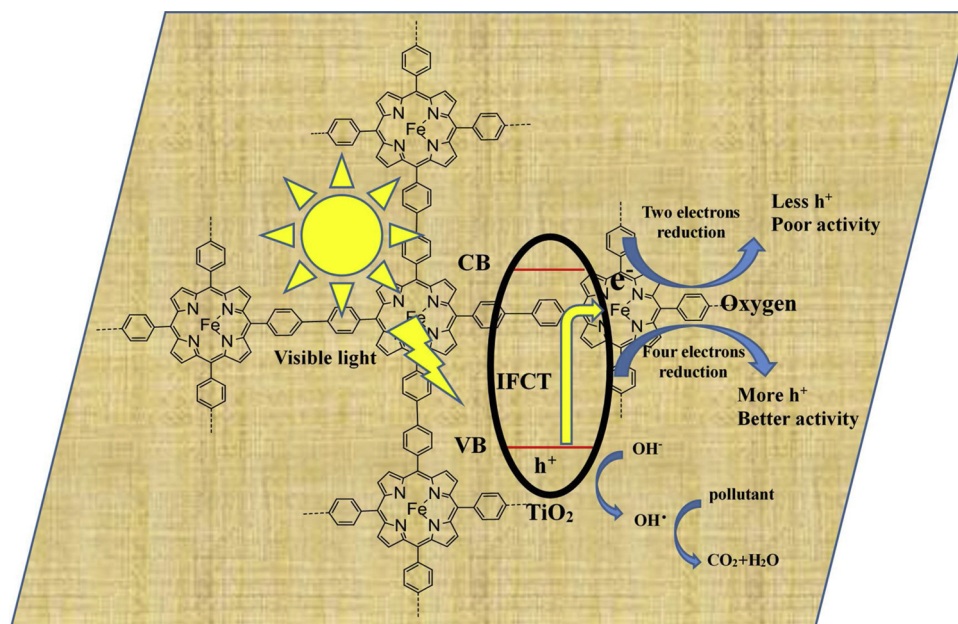


Fig. 10. Photocatalytic mechanism of  $\text{TiO}_2$ -FeCMP under visible light irradiation.

series, which was ascribed to the generation of photoinduced holes in the IFCT process. It could be found that the peaks intensity of  $\text{TiO}_2$ -FeCMP and  $\text{TiO}_2$ -FeCMP6 were higher than  $\text{TiO}_2$ -FeCMP0 and  $\text{TiO}_2$ -FeCMP18, which was consistent with the photocatalytic performance (Fig. S11), suggesting that four-electron oxygen reduction process might be better to accelerate the consumption of photoinduced electrons in the IFCT process than two-electron reduction, leaving more photoinduced holes in the valance band of  $\text{TiO}_2$  for further degradation, resulting in better photocatalytic activity.

The photocatalytic mechanism was proposed (Fig. 10). IFCT effect from the valance band of  $\text{TiO}_2$  to the Fe (III) in the FeCMP was triggered in the  $\text{TiO}_2$ -FeCMP compound under visible light irradiation. Meanwhile, the excited electrons were consumed on FeCMP through multi-electron ORR, which promoted IFCT effect. Further, it was revealed that four-electron oxygen reduction process was better to accelerate the consumption of photoinduced electrons than two-electron reduction in the IFCT process, leaving more photoinduced holes in the valance band of  $\text{TiO}_2$  for further degradation, resulting in better photocatalytic activity. Moreover,  $\text{TiO}_2$ -FeCMP showed great chemical stability after several times recycle (Fig. S16).

#### 4. Conclusion

In conclusion, FeP based CMPs were assembled on the surface of  $\text{TiO}_2$  microspheres to prepare an efficient visible-light-driven photocatalyst, where IFCT process was supposed to be the primary reason for the enhancement of photocatalytic performance under visible light irradiation. In addition, the relationship between IFCT effect and multi-electron ORR was claimed, and it was believable that four-electron oxygen reduction process was better able to accelerate the generation of photoinduced holes in the IFCT process, resulting in higher photocatalytic activity.

#### Conflict of interest

The authors declare no competing financial interest.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.03.075>.

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